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A detailed description

The present invention relates to the thermoplastic resin composite containing acrylic acid ester group elastomer, that has excellent weather resistance characteristic and anti impact characteristic.

As regards the 2-component type resin composite of elastomer - resin being marketed since past, ABS resin formed from acrylonitrile - butadiene - styrene is known, however, it has deteriorating weather resistance characteristic as it contains diene group elastomer possessing double bond, in its main chain and therefore, its outdoor applications are remarkably limited. Moreover, since the acrylic acid ester group elastomer has excellent weather resistance characteristic and anti thermal characteristic, it has not been used as the component of impact resistant resin replacing diene group elastomer, however, this elastomer does not contain unsaturated bond due to which it has low graft activity and moreover, modulus of elasticity is low

due to which composite having sufficient anti impact characteristic and other than that, mechanical properties and molding processibility has not been obtained. Generally, if the weather resistance characteristic of the 2-component resin composite formed from elastomer - resin is considered, weather resistance characteristic of elastomer can be reformed, however, if resin component is not taken into consideration, then excellent weather resistance possessed by the elastomer cannot be exhibited. As regards the resin component of such type of resin composite, styrene group resin (styrene more than 60 %) and methyl methacrylate group resin (methyl methacrylate more than 60 %) are widely used. If both these are seen from weather resistance aspect, both these have excellent weather resistance. The weather resistant resin formed by combining acrylic acid ester group elastomer and methyl methacrylate resin has been already proposed, however, its impact strength is low by a large magnitude as compared to that of the resin formed by using

styrene group resin. This is considered to be because the graft activity of methyl methacrylate with respect to acrylic acid ester group elastomer is low and the compatibility between this elastomer and methyl methacrylate is bad.

In order to obtain resin composite aiming at anti impact characteristic, weather resistance and excellent molding processibility from bridged acrylic acid ester group elastomer and resin component, different methods can be considered, however, if both these are physically mixed, compatibility between these two is unsatisfactory and therefore, composite having excellent properties is difficult to obtain. The authors of the present invention carried out an earnest research on this point as a result of which they showed that in order to obtained the desired resin composite using bridged acrylic rubber elastomer, at least 1 part among the resin component is required to be grafted and further, composite having excellent weather

resistance and anti impact strength can be obtained by combining acrylic acid ester group elastomer only with styrene, methyl methacrylate and acrylonitrile.

The present invention relates to the resin composite that is obtained by subjecting 3-component copolymer formed from 10 to 50 % by weight of methyl methacrylate, 5 to 40 % by weight of acrylonitrile or methacrylonitrile and less than 60 % by weight of styrene or α - methyl styrene, and the monomer formed from more than 60 % by weight of alkyl acrylate possessing alkyl radical having carbon atoms from 1 to 10, and less than 40 % by weight of at least 1 type of monomer chosen from acrylonitrile, methacrylonitrile, styrene, α - methyl styrene, methacrylic acid and alkyl methacrylate possessing alkyl radical having carbon atoms from 1 to 10, to the process of polymerization under the presence of bridging agent and then, (or) performing bridging treatment after carrying out polymerization and then, by blending the grafted copolymer formed by polymerizing 5 to 900 part of

monomer mixture formed from 10 to 50 % by weight of methyl methacrylate, 5 to 40 % by weight of acrylonitrile or methacrylonitrile and less than 60 % by weight of styrene or α - methyl styrene, under the presence of 100 part of bridged acrylic acid ester group elastomer having gel content of more than 80 % and degree of swelling within the range from 3 to 15, such that the content of elastomer becomes within the range from 5 to 40 %.

As regards the acrylic acid alkyl ester possessing alkyl radical having carbon atoms from 1 to 10 that composes the elastomer being used in the present invention, methyl methacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2 - ethyl hexyl acrylate etc. can be given. These can be used independently or by mixing more than 2 types. Moreover, the mixture of more than 60 % by weight, desirably, more than 75 % by weight of acrylic acid ester and less than 40 % by weight, desirably, less than 25 % by weight of at least 1 type chosen from acrylonitrile, methacrylonitrile,

styrene, α - methyl styrene, methacrylic acid or methacrylic acid alky ester possessing alkyl radical having carbon atoms from 1 to 10, can be used.

In the present invention, in the case of the acrylic acid ester group elastomer having gel content of less than 80 % and degree of swelling not within the range from 3 to 15, external appearance and molding processibility of the molded product gets deteriorated and dispersion of impact strength also becomes large which is not desired. As regards the bridging agent that is used for manufacturing the bridged acrylic acid ester group elastomer having gel content of more than 80 % and degree of swelling within the range from 3 to 15, organic peroxide as well as (or) multifunctional monomer possessing more than 2 units of conjugated double bond that is copolymerizable with the monomer composing elastomer can be used. As regards the examples of organic peroxides, benzoyl peroxide, lauroyl peroxide, 2, 4 - di chloro benzoyl peroxide etc. can be given and as regards the examples of

multifunctional monomer, ethylene glycol di methacrylate, tetra ethylene glycol di methacrylate, allylyl (?) methacrylate, di allylyl (?) phthalate, tri allylyl (?) cyanate, tri allylyl (?) iso cyanate etc. can be given.

The bridging reaction is carried out as mentioned below.

In the case of using organic peroxide, 0.3 to 3 parts by weight of peroxide is dissolved in 100 parts by weight of monomer composing acrylic acid ester group elastomer and emulsification polymerization is carried out using water soluble redox catalyst such as potassium peroxy di sulfate - sodium hydrogen sulfite, ammonium peroxy di sulfate - sodium thio sulfate etc., at a temperature at which the peroxide essentially does not get decompose, desirably, less than 50°C. Next, the bridging reaction is carried out in the latex state by carrying out heat treatment at a temperature of more than decomposition temperature of peroxide, desirably, more than 70°C. Or first monomer composing acrylic acid ester group elastomer is subjected to

emulsification polymerization by a usual method without making peroxide to co-exist and then, organic peroxide is dissolved in small quantity of monomer or water insoluble organic solvent such as methyl ethyl ketone, benzene etc. and then, latex is added to it after which peroxide is dispersed well in elastomer particles by stirring and then, bridging reaction is carried out by performing the same heat treatment. In the case of using multifunctional monomer as the bridging agent, 0.2 to 15 parts by weight of multifunctional monomer with respect to 100 parts by weight of monomer composing acrylic acid ester group elastomer is made to co-exist, and usual emulsification polymerization is carried out. Furthermore, in the case of using organic peroxide and multifunctional monomer jointly, either the monomer composing acrylic acid ester group elastomer is subjected to redox polymerization at the temperature at which the peroxide essentially does not get decomposed under the co-presence of both the bridging agents same as that in

case of using organic peroxide independently, or first emulsification polymerization is carried out only under the presence of multifunctional monomer and then, organic peroxide is dispersed in elastomer particles after which each of these latex is given heat treatment.

Regarding the resin component, if methyl methacrylate is present in a quantity of less than 10 % by weight, weather resistance does not become sufficient and satisfactory whereas if exceeds 50 % by weight, weather resistance is satisfactory, however, impact strength lowers. If the quantity of styrene in the process of copolymerization exceeds 60 % by weight, then there is no problem regarding impact strength, however, weather resistance lowers. If the quantity of acrylonitrile is less than 5 % by weight, then, there exists problem regarding impact strength, chemical resistance and anti thermal characteristic and on the other hand, if it exceeds 40 % by weight, then external appearance and molding characteristic get lowered.

In the practical examples, part and % relate to weight.

Practical example 1

(a) 200 part of de-ionized water containing 0.15 part of acidic soda sulfite was taken in a reaction vessel and nitrogen was blown for 30 minutes after which 0.3 part of potassium peroxy di sulfate was added to this aqueous solution at 35°C. After this, the mixture of 90 part of n - butyl acrylate prepared separately, 10 part of methyl methacrylate, 1 part of benzoyl peroxide and 2.4 part of perex (pelex ?) OTP (sulfo succinate group emulsifier, Hanao (Hanami ?) Atlas company make) was continuously added to the reaction system after nitrogen substitution for 2.5 hours. After the completion of addition, reaction was continued as it is for 30 minutes when generation of gel was not observed even the polymerization ratio reached to more than 95 % and 98 % of benzoyl peroxide was remained in the latex particles. Next, temperature inside the system was increased to 98°C and reaction was continued under stirring for 3 hours when

polymerization ratio became 98 % and the bridged elastomer latex having gel content of 95.1 % and degree of swelling of 9.8 was obtained. The gel content and degree of swelling are expressed by the following formula if the quantity of swelled film after immersing W_0 (quantity) of bridged acrylic acid ester group elastomer film in approximately 150 times weight of methyl ethyl ketone at 30°C for 24 hours, is taken as W_1 and quantity after absolute drying is taken as W_2 .

$$\text{Degree of swelling} = \frac{W_1 - W_2}{W_2}$$

$$\text{Gel content} = \frac{W_2}{W_0} \times 100 \ (\%)$$

305 part (solid part 100 part) of latex thus obtained was taken in a reaction vessel and temperature as increased to 70°C and stirring was carried out. The monomer mixture formed from 12 part of methyl methacrylate, 6 part of acrylonitrile and 12 part of styrene, and 0.15 part of potassium peroxo di sulfate dissolved in 5 part of ion exchange water were added to it. The reaction was completed in 1.5 hours and graft

polymer was obtained. Polymerization ratio was 99 %.

(b) 100 part of monomer mixture formed from acrylonitrile (AN), styrene (St) and methyl methacrylate (MMA) having composition as given in table 1, 0.35 part of lauryl mercaptan, 1 part of perex (pelex ?) OTP and 195 part of water taken in a reaction vessel and nitrogen substitution was carried out for 15 minutes after which solution of 0.13 part of potassium peroxy di sulfate in 5 part of water was added and polymerization was carried out at 60°C for 3 hours. Polymerization ratio was 94 ~ 98 %.

The resin latex thus obtained and graft latex obtained in (a) were blended such that the elastomer content becomes 25 % and the mixture was condensed by putting it in hot water (85 ~ 90°C) containing 2 % of approximately 3 times volume of aluminium chloride (crystals). Furthermore, it was given heat treatment at 90°C for 10 minutes and it was washed without using water and dried after which dried powder was pelletized by extruding at 200°C.

A flat plate of 110 x 110 x 2 mm (gate 1.2 φ, pinpoint) was molded from this pellet using an injection molding machine (Nikko (?) V - 14 - 65 model, inline screw type) and difficult physical properties were evaluated. These results have been presented in table 1 given below. In table, test material A is the material of the present invention and B is that of comparative example. Impact strength shows dyne stat (?) impact strength measured by DIN 53453. Moreover, weather resistance shows the time required for the impact strength of the test material to become 50 % of the initial by hitting from the exposed surface of the test material using accelerated exposure machine (Toyo Rika (Toyo Scientific) WE - II model). Furthermore, thermal deformation temperature was measured by ASTM D - 648 - 56.

Table 1

Test material	AN/St/MMA (%) by weight)	Impact strength (kg)	Weather resistance (hours)	Thermal deformation temperature

		cm/cm ²)		(°C)
A - 1	10/45/45	60 - 75	800	86
B - 1	10/70/20	65 - 90	300	89
B - 2	10/30/60	15 - 35	850	-
A - 2	20/45/35	85 - 106	750	90
A - 3	20/40/40	88 - 106	800	88
A - 4	20/35/45	70 - 90	800	88
B - 3	20/20/60	12 - 30	900	87
B - 4	20/70/10	85 - 110	300	92
A - 5	25/30/45	76 - 90	850	89
A - 6	25/40/35	90 - 101	800	90
A - 7	25/45/30	90 - 108	700	91
A - 8	25/50/25	98 - 103	700	89
B - 5	25/15/60	15 - 32	800	-
B - 6	25/75/0	100 - 106	250	93
A - 9	30/30/40	70 - 92	800	90
A - 10	30/40/30	90 - 100	700	91
B - 7	30/10/60	15 - 25	800	-
B - 8	30/65/5	88 - 106	250	94

A - 11	35/35/30	60 - 86	700	91
B - 9	35/10/55	20 - 90	50	86
ABS	High impact type	75 - 90	50	86

As is clear from the table, only in range of AN/MMA / St specified by the present invention, composite having excellent impact strength and weather resistance can be obtained.

Practical example 2

200 part of de-ionized water was taken in a reaction vessel and nitrogen was blown for 30 minutes after which 0.3 part of potassium peroxy di sulfate was added. After this, 10 part of the mixture of 90 part of n - butyl acrylate prepared separately, 6 part of methyl methacrylate, 4 part of ethylene glycol di methacrylate and 2.4 part of perex (pelex ?) OTP was kept aside and other part was continuously added to the reaction system for 120 minutes. After the completion of addition, reaction was continued for 30 minutes. Next,

temperature of the reaction system was reduced to 40⁰C and the solution formed by dissolving 1 part of benzoyl peroxide in the remaining 10 part the mixture mentioned above was added to the reaction system and it was stirred for 60 minutes. Next, temperature was increased to 98⁰C and reaction was further continued under stirring for 3 hours when the polymerization ratio reached 99 % when bridged elastomer latex having gel content of 96.0 % and degree of swelling of 5.8 was obtained.

Nitrogen substitution was carried out in this latex and 400 part of de-ionized water was added and the system was maintained at 70⁰C after which the mixture formed from 80 part styrene prepared separated under nitrogen current, 80 part of methyl methacrylate, 40 part of acrylonitrile and 1 part of benzoyl peroxide was continuously dropped into the reaction system for 4 hours and polymerization was carried out. After the completion of dropping, temperature was increased to 80⁰C and reaction was continued for 30 minutes

when the polymerization ratio of the obtained latex polymer was 99.8 %.

The latex polymer thus obtained and resin latex A - 3 obtained in practical example 1 were blended such that the content of elastomer becomes 25 % and molded product was obtained by carrying out operation similar to that of practical example 1. Dyne state impact strength of the obtained molded product was 110 ~ 105 kg cm / mc² and weather resistance was 800 hours.

Practical example 3

As regards the monomer composing acrylic acid ester group elastomer, 30 part of ethyl acrylate, 60 part of n - butyl acrylate, 5 part of α - methyl styrene and 5 part of methyl methacrylate were used. Other than this change, reaction similar to that of practical example 1 was carried out and bridged elastomer latex having gel content of 93 % and degree of swelling of 9.5 was obtained. This was used and graft copolymer latex was prepared by carrying out the reaction

similar to that of practical example 1.

Resin A - 3 of practical example 1 was prepared separately and here, α - methyl styrene was used instead of styrene and resin polymer latex was synthesized. This was blended with graft polymer latex mentioned above such that content of elastomer becomes 25 %. The impact strength of this resin composite was $80 \sim 96 \text{ kg cm / mc}^2$ and weather resistance was 700 hours.

Practical example 4

The mixture formed from 80 part of n - butyl acrylate, 20 part of n - butyl methacrylate, 0.5 part of tri allylyl (?) iso cyanate and 3 part of perex (pelex ?) OTP was added to 200 part of aqueous solution containing 0.3 part of potassium peroxy di sulfate maintained at 70°C in 2 hours. After the completion of addition, reaction was continued at 85°C for 1 hours when bridged elastomer latex having gel content of 94.1 % and degree of swelling of 8.9 was obtained. 6 part of methacrylonitrile, 12 part of styrene and 12 part of

methyl methacrylate were graft polymerized at 70⁰C using 0.15 part of potassium peroxy di sulfate under the presence of this latex.

After this, resin polymer latex was synthesized separately using methacrylonitrile, styrene and methyl methacrylate in a proportion same as mentioned above and this was blended with graft polymer latex such that the content of elastomer becomes the value given in table 2. When these were evaluated for physical properties same as that of practical example 1, results given in table 2 were obtained.

Table 2

Elastomer content (%)	Impact strength (kg cm/cm ²)	Thermal deformation temperature (°C)	Tensile strength (kg/cm ²)	Weather resistance (hours)
25	80 - 105	93	405	800
20	65 - 93	94	463	"
15	15 - 40	96	508	750
10	6 - 20	99	583	800

5	4 - 7	105	625	850
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(57) Scope of patent claims

1. Resin composite that is obtained by subjecting 3-component copolymer formed from 10 to 50 % by weight of methyl methacrylate, 5 to 40 % by weight of acrylonitrile or methacrylonitrile and less than 60 % by weight of styrene or α - methyl styrene, and the monomer formed from more than 60 % by weight of alkyl acrylate possessing alkyl radical having carbon atoms from 1 to 10, and less than 40 % by weight of at least 1 type of monomer chosen from acrylonitrile, methacrylonitrile, styrene, α - methyl styrene, methacrylic acid and alkyl methacrylate possessing alkyl radical having carbon atoms from 1 to 10, to the process of polymerization under the presence of bridging agent and then, (or) performing bridging treatment after carrying out polymerization and then, by blending the grafted copolymer formed by polymerizing 5 to 900 part of monomer mixture formed from 10 to 50 % by weight of methyl methacrylate, 5

to 40 % by weight of acrylonitrile or methacrylonitrile and less than 60 % by weight of styrene or α - methyl styrene, under the presence of 100 part of bridged acrylic acid ester group elastomer having gel content of more than 80 % and degree of swelling within the range from 3 to 15, such that the content of elastomer becomes within the range from 5 to 40 %.